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COMPLETE SPECIFICATION

A Process for the Production of Cellular Bodies

WE, ZELLSTOFFFABRIK WALDHOF, a German Body Corporate, of 156, Sandhoferstrasse, Mannheim-Waldhof, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention concerns a process for the production of cellular bodies from natural rubber, synthetic rubber, polyisoolefines and other elastomers, with addition of lignin products.

Cellular bodies are used more and more in technical science and in everyday life. They consist of elastic products which are inflated and enlarged by pores and by occlusion of gas. Owing to their special structure, they possess, in addition to a small weight by volume as compared with solid rubber, the advantages of insulating and damping properties and therefore can be used particularly favourably for numerous purposes.

Cellular bodies are obtained in two different ways. Either there is added to the starting material, for example crude rubber, a gas-producing material, such as pentamethylenetetramine, which at elevated temperature, as in the case of vulcanisation, decomposes with evolution of gases and so inflates the rubber, or the rubber composition is treated before, during or after the vulcanisation with an inert gas, for example nitrogen, under increased pressure. The existing processes, however, could not completely satisfy. When working with inert gas it has not seemed possible to prepare cellular bodies from elastomers greatly diluted by means of fillers. On the contrary, one started from the pure raw materials, such as rubber. The products so produced were of course expensive. Moreover, there was little possibility of varying the properties of the products by the addition of fillers.

Again, when using gas-producing agents, satisfactory products, which after the heat

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treatment did not show any contraction and consequent destruction of their structure, hitherto could only be prepared with relatively large additions of inorganic fillers. To this end, when using reinforcing fillers of high reinforcing effect, such as silicic acid and aluminium silicate, at least 30% was necessary, and when using fillers having a smaller reinforcing effect, such as kaolin, chalk and heavy spar, at least 50% was required. Due to this, the specific gravity of the products was undesirably high. Moreover, the possibilities of varying the properties of the products were substantially restricted.

It has now been found that it is possible to prepare in a simple way cheap expanded cellular bodies of outstanding qualities from natural rubber, synthetic rubber, polyisoolefines and other elastomers, if the elastomer is admixed with a lignin product as hereinafter defined together with a solvent for said elastomer having a boiling point higher than the vulcanisation temperature of said elastomer, and/or a plasticiser without including in said mixture any inorganic filler in excess of 20% by weight of the elastomer, and the mixture is thereafter converted in known manner into an expanded cellular body. In this manner it possible to produce in a satisfactory way cellular bodies of outstanding qualities which, owing to the admixture of considerable portions of lignin, are very cheap. The products so obtained are distinguished above all by a very small specific gravity. Moreover, the possibility exists according to the invention of improving the structural characteristics of the products obtained by the addition of the lignin substance. When using gas-producing agents, there is, besides, the advantage of being able to manage without the addition of relatively large amounts of inorganic fillers.

By "lignin products" we mean the products of chemical digestion of lignin-containing raw materials, in particular products

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containing ligninsulphonic acid or its compounds, such as sulphite cellulose waste liquor. This spent liquor may be used as such (after evaporating down and preferably drying) or also after conversion to other forms, for example by precipitation with lime or by fermentation.

The mixing of the lignin product with the elastic material may take place in any way, e.g. in a kneader or on a roller. The proportion of lignin product added can also be greatly varied. Additions between 50% and 150% have proved particularly suitable.

Lignin products have already been used as fillers for solid rubber. In addition to the filling action, the structural stability and above all the hardness of the end product were also improved by this means. It was therefore all the more surprising that, in the case of products such as cellular bodies whose structure is opened up by the action of gases, it was possible, by the addition of lignin products, even in fairly large amount, to produce in a satisfactory way and without introducing any production difficulties products with outstanding qualities.

In particular, it was unexpectedly possible by means of the invention to produce cellular bodies from compositions filled to a great extent with lignin products under the action of gases introduced at high pressure. It was previously not possible to convert satisfactorily into cellular bodies in this way compositions containing substantially more than 20% of fillers, since such compositions opposed the action of the gas in the desired way.

The invention allows products to be produced with widely differing properties dependent upon the intended purpose of use and the characteristics therefore required of the products. It is possible, for example, by the addition of the lignin product and without use of other fillers, to prepare cellular bodies of great hardness without destruction of the structure of the material taking place during the inflating process. Up to 20% (with respect to the weight of elastomer) of inorganic fillers, such as carbon black and aluminium silicate, may also be added, however, apart from the lignin product employed, and the properties of the end products may be extensively varied by this means. In this connection zinc oxide is not to be understood as a filler, at least when it is used in amounts which do not exceed that required for the activation.

Special difficulties have had to be overcome since the mixing of the lignin product with the elastomer gave rise to complications. It appeared that the use of the usual solvents, such as water, lower alcohols of low boiling point or similar organic solvents, during the inflating process caused trouble owing to shrinking so that satisfactory cel-

lular bodies were not obtained. It was found possible to overcome these difficulties and to obtain satisfactory products if solvents for the elastomers having higher boiling points than the vulcanisation temperature of the elastomer employed, preferably lower polyhydroxy alcohols such as glycol or glycerine, and/or plasticisers, suitably mineral oil products and preferably those containing preponderantly saturated hydrocarbons, such as, for example, Naftolen, are mixed, together with the lignin product, with the elastomer. The amount of the solvent and/or plasticiser depends upon the product desired and may vary within wide limits. Usually 5-20% by weight, calculated on the lignin product, is suitable.

If a gas-producing agent is used, its amount is calculated in the usual way according to the amount of the elastomer and usually equals between 3% and 10% of the latter.

If an inert gas is used for forming the structure, it can be used before, during or after the vulcanisation. It has been found that the compositions obtained according to the invention, even with a high lignin content, also show thermoplastic behaviour in the vulcanised state at elevated temperature, and by the action of one or more gases under pressure form inflated products with a uniform cellular structure.

The products obtained are capable of further modifications in the usual manner. Thus by increasing the sulphur content, products having a character similar to that of hard rubber can be produced.

The products obtained according to the invention have a uniform cellular structure and a smooth surface. They display good elastic properties, good stability of structure, good wearing properties and low specific gravity. Moreover, the lignin has a strengthening effect upon the properties of the products.

The cellular bodies obtained are excellently suited, depending upon the mixing proportions and the other conditions of the preparation, as insulating and damping material, in the manufacture of upholstery, mats and shoe soles, and for numerous other purposes.

The following three compositions were prepared:

I. 70 parts of a lignin product obtained by evaporating and drying fermented pinewood-sulphite spent liquor from the manufacture of paper pulp are mixed at 80°C. with 1.5 parts of glacial acetic acid, 4 parts of paraformaldehyde, 25 parts of glycerine and 6 parts of aniline oil.

II. 70 parts of a lignin product obtained by evaporating and drying unfermented pinewood-sulphite spent liquor from the manufacture of paper pulp are mixed at

80°C. with 1.5 parts of glacial acetic acid, 4 parts of paraformaldehyde, 25 parts of ethylene glycol and 6 parts of aniline oil.

III. 100 parts of a lignin product obtained 5 by evaporating and drying unfermented beech-sulphite spent liquor from the manufacture of paper pulp are mixed at 80°C. with 1.5 parts of glacial acetic acid, 4 parts of paraformaldehyde, 55 parts of a mineral 10 oil product containing preponderantly unsaturated hydrocarbons and 6 parts of aniline oil.

With the compositions prepared as above cellular bodies are then produced according 15 to the following examples:

EXAMPLE 1.

430 parts of composition I, II or III are mixed in the kneader with 430 parts of natural rubber (Remilled smoked sheet): 200 20 parts of polyisobutylene with a molecular weight of about 1500, 35 parts of antimony pentasulphide, 35 parts of ozokerite, 35 parts of magnesium carbonate, 35 parts of sulphur and 35 parts of a mineral oil with 25 a high content of unsaturated hydrocarbons (Naftolen ZD) are mixed with the batch so obtained. The mixture is pre-vulcanised for an hour at 125°C. and afterwards treated with nitrogen under 600 atm. pressure for 30 2½ hours at 125°C. It is finally cooled for 3 hours. There is obtained a well dilated cellular body with closed pores and a specific gravity of about 0.1, and of very good mechanical properties.

EXAMPLE 2.

500 parts of composition I, II or III are mixed in the kneader with 500 parts of synthetic rubber (that sold under the Registered Trade Mark Buna S 3, broken down). With 40 the batch so obtained are mixed 25 parts of active zinc oxide, 10 parts of stearic acid, 12.5 parts of sulphur, 5 parts of mercaptobenzthiazole, 2.5 parts of diphenylguanidine and 25 parts of benzenesulphonic acid hy- 45 drazide. The mixture is heated at 142°C. for 20 minutes in the press. The product obtained is a cellular body of specific gravity 0.25 having excellent mechanical properties.

EXAMPLE 3.

530 parts of composition I, II or III are mixed in the kneader with 530 parts of natural rubber (remilled crepe). With the batch thus obtained are mixed 230 parts of synthetic rubber (that sold under the Registered Trade Mark Buna SS, broken down), 55 13 parts of stearic acid, 43 parts of zinc oxide, 10 parts of phenyl β-naphthylamine, 43 parts of magnesium carbonate and 17 parts of tetramethylthiuram disulphide. The 60 mixture is prevulcanised at 125°C. for an

hour and then treated with nitrogen under 600 atm. pressure at 125°C. for 2½ hours. It is finally cooled for 3 hours. The product obtained is a cellular body of specific gravity 0.09 having uniformly closed pores and excellent mechanical properties.

WHAT WE CLAIM IS:—

1. A process for the production of expanded cellular bodies from natural rubber, synthetic rubber, polyisoolefines and other 70 elastomers, comprising mixing said elastomer with a lignin product as hereinbefore defined and a solvent for said elastomer having a boiling point higher than the vulcanization temperature of said elastomer, and/or 75 a plasticiser, without including in the resulting mixture any inorganic filler in excess of 20% by weight of the elastomer, and thereafter converting the mixture in known manner into an expanded cellular body. 80

2. A process as claimed in Claim 1, in which the lignin product contains lignin sulphonic acid or a compound thereof.

3. A process as claimed in either of Claims 1 and 2, in which the quantity of 85 lignin product is within the range 50-150% by weight with respect to the elastomer.

4. A process as claimed in any of the preceding claims, in which the mixture contains no inorganic filler. 90

5. A process as claimed in any of Claims 1 to 3, in which the mixture contains carbon black or aluminium silicate as inorganic filler.

6. A process as claimed in any of the 95 preceding claims, in which the solvent is a lower polyhydroxy alcohol, e.g. glycol or glycerine.

7. A process as claimed in any of the preceding claims, in which the plasticiser is 100 a mineral oil product.

8. A process as claimed in Claim 7, in which the mineral oil product contains a preponderant amount of unsaturated hydrocarbons. 105

9. A process as claimed in any of the preceding claims, in which a gas-producing agent is also incorporated in said mixture.

10. A process as claimed in any of Claims 1 to 8, in which the mixture is converted 110 into a cellular body before, during or after vulcanization by the action of one or more gases under increased pressure.

11. Processes for the production of cellular bodies, substantially as hereinbefore described in Examples 1 to 3. 115

W. P. THOMPSON & CO.,

12 Church Street,

Liverpool, 1,

Chartered Patent Agents.

